

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 3/20, 11/00, 3/39	A1	(11) International Publication Number: WO 97/38074 (43) International Publication Date: 16 October 1997 (16.10.97)
(21) International Application Number: PCT/EP97/01287 (22) International Filing Date: 12 March 1997 (12.03.97) (30) Priority Data: 96200935.3 10 April 1996 (10.04.96) EP <i>(34) Countries for which the regional or international application was filed:</i> NL et al. (71) Applicant (for all designated States except AU BB CA GB IE KE LK LS MN MW NZ SD SG SZ TT UG): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). (71) Applicant (for AU BB CA GB IE KE LK LS MN MW NZ SD SG SZ TT UG only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (72) Inventor: KOEK, Jean, Hypolites; Unilever Research Vlaardingen Laboratory, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). (74) Common Representative: UNILEVER N.V.; Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: CLEANING PROCESS (57) Abstract A process is disclosed for cleaning of a substrate, comprising the steps of (1) adding a molecular oxygen activating system (as defined herein) to an aqueous wash liquor, containing a sufficient amount of molecular oxygen for obtaining observable cleaning, and (2) cleaning the substrate with the thus-formed wash liquor. When using said process, significant substrate cleaning results could even be obtained in the absence of any usually applied active oxygen ingredient such as perborate or percarbonate.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

CLEANING PROCESSField of the invention

5 The invention relates to a process for cleaning of a substrate, wherein molecular oxygen is applied. In particular, the present invention is concerned with the novel use of a molecular oxygen activating system in said cleaning process.

10

Background of the invention

To accomplish stain removal from substrates, such as fabric substrates, peroxide bleaching agents, such as hydrogen peroxide or peracids, are generally used as active oxygen
15 ingredients. Such bleaching agents for use in laundering have been known for many years.

These types of active oxygen ingredients are particularly effective in removing stains, such as tea, fruit and wine stains, from clothing, when used in combination with
20 peracid precursors and/or bleach catalysts.

We have now looked at alternative routes for achieving stain removal. First of all, the molecular oxygen present in the wash liquor was considered. It was however found
25 that said molecular oxygen was not sufficiently effective as such for achieving any observable cleaning result; some form of activation appears to be needed for accomplishing bleaching action.

30 Accordingly, it is an object of the present invention to provide a cleaning result by applying a process in which molecular oxygen is activated and effectively used for cleaning purposes. It is an other object to provide a cleaning process which is cost-effective and
35 environmentally acceptable. It is a further object to

provide a cleaning process which improves hygiene and/or reduces dye transfer.

It was surprisingly found that a cleaning benefit could be obtained by applying a simple process wherein a molecular oxygen activating system is added to an aqueous wash liquor containing a sufficient amount of molecular oxygen for obtaining observable cleaning, and a substrate is treated with the thus-obtained wash liquor. In view of the kinetic inertness of the molecular oxygen as such and its low equilibrium concentration in aqueous solutions, it was not expected that observable substrate cleaning performance could be obtained when applying this process. Significant substrate cleaning and bleaching results could even be obtained in the absence of any usually applied active oxygen ingredient such as perborate, percarbonate or peracids.

In this respect, molecular oxygen is defined as dioxygen in the $^3\Sigma_g^-$ triplet ground state. Furthermore, in the context of the present invention, a molecular oxygen activating system is defined as a system which activates molecular oxygen (as defined above) resulting in an observably more efficient reaction with a substrate than would be obtained without said system. In other words, the activating system is defined as a compound or mixture of compounds which interacts with molecular oxygen and thereby increases or induces reactivity between said molecular oxygen and a substrate.

Definition of the invention

Accordingly, in one aspect the present invention provides a process for cleaning of a substrate, comprising the steps of (1) adding a molecular oxygen activating system (as defined herein) to an aqueous wash liquor, containing a sufficient amount of molecular oxygen for obtaining observable cleaning, and (2) cleaning the substrate with the thus-formed wash liquor.

In another aspect, the present invention provides the use of a molecular oxygen activating system for cleaning of a substrate, whereby said activating system is added to an aqueous wash liquor containing a sufficient amount of
5 molecular oxygen for obtaining observable cleaning, and the substrate is cleaned using the thus-formed wash liquor.

Detailed description of the invention

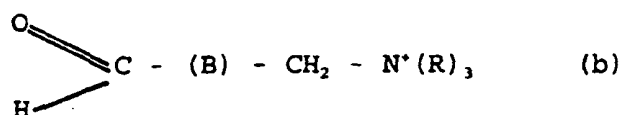
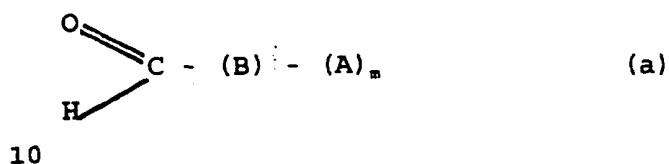
The obtained cleaning effect as a result of the process of
10 the present invention, which was measured in terms of its bleaching performance, was surprising and unexpected. For obtaining noticeable cleaning result, only a small amount of molecular oxygen was found to be required. Preferably, at least 0.01 mMol O₂ per litre of aqueous wash
15 liquor is used in the process of the invention. Said molecular oxygen can be supplied as pure molecular oxygen gas or as molecular oxygen - containing gas such as air. The molecular oxygen can be effectively supplied to the aqueous wash liquor, for instance by bubbling it through
20 said liquor or by shaking said liquor. Alternatively, the molecular oxygen can be generated in situ by electrochemical, chemical or enzymatic reactions.

The process of the invention is generally carried out at a
25 temperature between 0-90°C, preferably in the range of 20-60°C. To obtain the desired bleaching result, the pH of the wash liquor is preferably in the range of 4-12, more preferably in the range of 7-10.

30 The substrate to be cleaned by the process of the invention may generally be any substrate, such as hard surfaces, for instances floor surfaces, dishes and fabric. However, the process of the invention is preferably applied for cleaning fabric substrates.

The aldehyde

The molecular oxygen activating system according to the present invention preferably includes from 0.01 to 40 mMol/litre, based on the volume of the wash liquor, of at least one aldehyde according to the formulas (a) or (b):

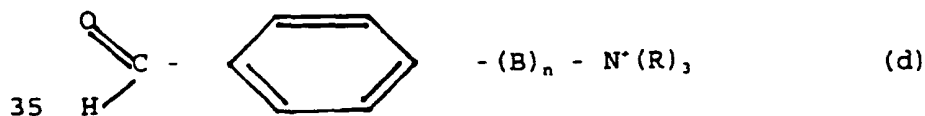
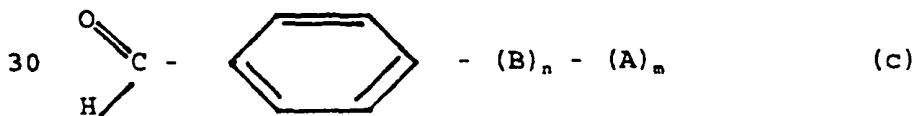


15 wherein:

A is selected from sulphate, sulphonate, phosphate, carboxylate, nitro, amine, or a quaternary ammonium group; B and R are independently selected from C₁ - C₁₀, branched or linear, substituted or unsubstituted alkyl, polyethoxy

20 alkyl, hydroxyalkyl or an aromatic group selected from substituted or unsubstituted benzene, naphthalene, pyrrole, furane, thiophene, imidazole, pyrazole, pyridine, pyrimidine, indole or benzimidazole; and m is an integer which may be 0 or 1.

25 More preferably, the aldehyde present in the preferred molecular oxygen activating system is an aromatic aldehyde according to the formulas (c) or (d):



wherein A, B, R, and m are defined as indicated above, and n is an integer which may be 0 or 1.

While not wishing to be bound by theory, it is considered that the following mechanism is likely to unexpectedly occur during the process of the invention, when the activating system includes an aldehyde: even in the absence of any bleach catalysts, bleach precursors, or radical initiators, a small steady state quantity of peracid is probably formed which appears to be bleach active at the low concentrations applied in the wash liquor.

The concentration of the aldehyde in the aqueous wash liquor is desirably 0.5-30 mmol/liter, a concentration of 1-15 mmol/liter being most preferred.

A surprisingly large bleaching result was observed when using substituted aromatic aldehydes which is a compound according to formula (c) wherein m is 0, n is 1, and B is a C₁-C₅ branched or linear, alkyl or alkoxy group. These types of substituted aromatic aldehydes are therefore most preferred. The para-methyl and para-ethyl benzaldehyde were found to give the highest bleaching activity.

Other constituents of the molecular oxygen activating system

It was found that the observed substrate cleaning performance could be improved by addition to the wash liquor of a radical initiator, being a compound which can initiate chemical reactions by producing free radicals. A number of such compounds are mentioned in Kirk-Othmer, "Encyclopedia of Chemical Technology, 4th edition, volume 14, page 431-460. A suitable example of such a radical initiator is dibenzoyl peroxide (BPO). Other examples are tertiary butylperoxy acetate, ditertiary butylperoxide, potassium peroxydisulphate and azo-bis-isobutyronitril. Another class of radical initiators are compounds which give free radicals upon reaction with air. This type of

radical initiators are described by Y. Ishii, J.Org.Chem. 22, (1995) 3934-3935. A suitable example is N-hydroxy succinimide (NHS).

Another example is N-hydroxy-benzimidazole.

- 5 The preferred concentration of the radical initiator in the wash liquor is 0.1 - 2 mMol/liter.

The observed bleaching performance could also be improved by the addition to the wash liquor of a transition metal
10 complex. The preferred concentration thereof in the wash liquor is in the range of 0.1-20 microMol/liter.

Preferred transition metal complexes are complexes of manganese, iron, cobalt, molybdenum or tungsten. More preferred are complexes of iron or manganese containing
15 ligands, so as to result in hydrolytically stable complexes.

Examples are manganese complexes having, as a ligand, an 1,4,7-trimethyl-1,4,7-triazacyclononane structure (as disclosed by EP-A-458,397) and ligand containing iron
20 complexes wherein the ligand is N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)-methylamine (as disclosed by WO 95/34628).

Another group of compounds which can improve the bleaching
25 performance are the transition metal containing enzymes, for instance the peroxidases.

Wash liquor composition

In addition to the molecular oxygen activating system of
30 the present invention, the aqueous wash liquor may contain the usual ingredients of a detergent composition such as peroxy bleaching compounds, surfactants, and builders.

The peroxy bleaching compound

35 Although not needed for obtaining the desired fabric bleaching effect, the wash liquor may contain a peroxy

bleaching agent, at a concentration of from 0.01 to 20 mMol/liter.

The peroxy bleaching compound may be a compound which is capable of yielding hydrogen peroxide in aqueous solution. Hydrogen peroxide sources are well known in the art. They include the alkali metal peroxides, organic peroxides such as urea peroxide, and inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Mixtures of two or more such compounds may also be suitable.

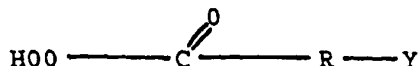
Particularly preferred are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because of its high active oxygen content. Sodium percarbonate may also be preferred for environmental reasons.

Another suitable hydrogen peroxide generating system is a combination of a C₁-C₄ alkanol oxidase and a C₁-C₄ alkanol, especially a combination of methanol oxidase (MOX) and ethanol. Such combinations are disclosed in International Application PCT/EP 94/03003 (Unilever), which is incorporated herein by reference.

25

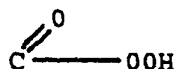
Alkylhydroxy peroxides are another class of peroxy bleaching compounds. Examples of these materials include cumene hydroperoxide and t-butyl hydroperoxide.

Organic peroxyacids may also be suitable as the peroxy bleaching compound. Such materials normally have the general formula:



35

wherein R is an alkylene or substituted alkylene group containing from 1 to about 20 carbon atoms, optionally having an internal amide linkage; or a phenylene or substituted phenylene group; and Y is hydrogen, halogen, alkyl, aryl, an imido-aromatic or non-aromatic group, a COOH or



group or a quaternary ammonium group.

Typical monoperoxy acids useful herein include, for example:

- (i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy- α -naphthoic acid;
- (ii) aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, e.g. peroxy lauric acid, peroxy stearic acid and N,N-phthaloylaminoperoxy caproic acid (PAP); and
- (iii) 6-octylamino-6-oxo-peroxyhexanoic acid.

Typical diperoxyacids useful herein include, for example:

- (iv) 1,12-diperoxydodecanedioic acid (DPDA);
- (v) 1,9-diperoxyazelaic acid;
- (vi) diperoxybrassicic acid; diperoxysebacic acid and diperoxyisophthalic acid;
- (vii) 2-decyldiperoxybutane-1,4-dioic acid; and
- (viii) 4,4'-sulphonylbis(peroxybenzoic acid).

Also inorganic peroxyacid compounds are suitable, such as for example potassium monopersulphate (MPS).

All these peroxy compounds may be utilized alone or in conjunction with a peroxyacid bleach precursor and/or an organic bleach catalyst not containing a transition metal.

Peroxyacid bleach precursors are known and amply described in literature, such as in the British Patents 836988; 864,798; 907,356; 1,003,310 and 1,519,351; German Patent 3,337,921; EP-A-0185522; EP-A-0174132; EP-A-0120591; and US
5 Patents 1,246,339; 3,332,882; 4,128,494; 4,412,934 and 4,675,393.

Another useful class of peroxyacid bleach precursors is that of the cationic i.e. quaternary ammonium substituted
10 peroxyacid precursors as disclosed in US Patent 4,751,015 and 4,397,757, in EP-A0284292 and EP-A-331,229. Examples of peroxyacid bleach precursors of this class are:
2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphonphenyl carbonate chloride - (SPCC);
15 N-octyl,N,N-dimethyl-N₁₀-carbophenoxy decyl ammonium chloride - (ODC);
3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and
N,N,N-trimethyl ammonium toluyloxy benzene sulphonate.

20

A further special class of bleach precursors is formed by the cationic nitriles as disclosed in EP-A-303,520 and in European Patent Specification No.'s 458,396 and 464,880.

25 Any one of these peroxyacid bleach precursors can be used in the present invention, though some may be more preferred than others.

Of the above classes of bleach precursors, the preferred
30 classes are the esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors including the cationic nitriles.

35 Examples of said preferred peroxyacid bleach precursors or activators are sodium-4-benzoyloxy benzene sulphonate

(SBOBS); N,N,N',N'-tetraacetyl ethylene diamine (TAED); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate; SPCC; trimethyl ammonium toluoyloxy-benzene sulphonate; sodium nonanoyloxybenzene
5 sulphonate (SNOBS); sodium 3,5,5-trimethyl hexanoyl-oxybenzene sulphonate (STHOBS); and the substituted cationic nitriles.

Surfactants

- 10 The aqueous wash liquor may generally contain a surface-active material in an amount up to 3 grams/liter. Said surface-active material may be naturally derived, such as soap, or a synthetic material selected from anionic, nonionic, amphoteric, zwitterionic, cationic actives and
15 mixtures thereof. Many suitable actives are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.
- 20 Typical synthetic anionic surface-actives are usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher aryl radicals. Examples
25 of suitable synthetic anionic detergent compounds are sodium and ammonium alkyl sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols produced, for example, from tallow or coconut oil; sodium and ammonium alkyl (C_9-C_{19}) benzene sulphonates, particularly
30 sodium linear secondary alkyl ($C_{10}-C_{15}$) benzene sulphonates; sodium alkyl glyceryl ether sulphates, especially those ester of the higher alcohols derived from tallow or coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and ammonium salts of sulphuric acid esters of
35 higher (C_9-C_{18}) fatty alcohol alkylene oxide, particularly ethylene oxide, reaction products; the reaction products of

fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and ammonium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by
5 reacting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived by reaction paraffins with SO_2 and C_{12} and then hydrolysing with a base to produce a random sulphonate; sodium and ammonium C_7-C_{12} dialkyl sulphonates; and olefin sulphonates which term is used
10 to describe material made by reacting olefins, particularly $C_{10}-C_{20}$ alpha-olefins, with SO_2 and then neutralising and hydrolysing the reaction product. The preferred anionic detergent compounds are sodium ($C_{10}-C_{15}$) alkylbenzene sulphonates, sodium ($C_{16}-C_{18}$) alkyl ether sulphates.

15

Examples of suitable nonionic surface-active compounds which may be used, preferably together with the anionic surface-active compounds, include, in particular, the reaction products of alkylene oxides, usually ethylene
20 oxide, with alkyl (C_6-C_{22}) phenols, generally 5-25 EO, i.e. 5-25 units of ethylene oxides per molecule; and the condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 2-30 EO. Other so-called nonionic surface-
25 actives include alkyl polyglycosides, sugar esters, long-chain tertiary amine oxides, long-chain tertiary phosphine oxides and dialkyl sulfoxides.

Amphoteric or zwitterionic surface-active compounds can
30 also be used in the compositions of the invention but this is not normally desired owing to their relatively high cost. If any amphoteric or zwitterionic detergent compounds are used, it is generally in small amounts in compositions based on the much more commonly used synthetic anionic and
35 nonionic actives.

Builders

The wash liquor may also contain a detergency builder, in an amount of up to 4 grams/liter.

Builder materials may be selected from 1) calcium

- 5 sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium

- 10 tripolyphosphate; nitrilotriacetic acid and its water-soluble salts; the alkali metal salts of carboxymethyloxy succinic acid, ethylene diamine tetraacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, citric acid; and polyacetal carboxylates as
15 disclosed in US Patents 4,144,226 and 4,146,495.

Examples of precipitating builder materials include sodium orthophosphate and sodium carbonate.

- 20 Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best known representatives, e.g. zeolite A, zeolite B (also known as Zeolite P), zeolite C, zeolite X, zeolite Y and also the
25 zeolite P type as described in EP-A-384,070.

- In particular, the compositions of the invention may contain any one of the organic and inorganic builder materials, though, for environmental reasons, phosphate
30 builders are preferably omitted or only used in very small amounts.

Typical builders usable in the present invention are, for example, sodium carbonate, calcite/carbonate, the sodium salt of nitrilotriacetic acid, sodium citrate,

- 35 carboxymethyloxy malonate, carboxymethyloxy succinate and the water-insoluble crystalline or amorphous

aluminosilicate builder material, each of which can be used as the main builder, either alone or in admixture with minor amounts of other builders or polymers as co-builder.

5 Other ingredients of the wash liquor

Apart from the components already mentioned, the wash liquor can contain any of the conventional additives in amounts of which such materials are normally employed when cleaning substrates such as fabric substrates.

- 10 Examples of these additives include buffers such as carbonates, lather boosters, such as alkanolamides, particularly the monoethanol amides derived from palmkernel fatty acids and coconut fatty acids; lather depressants, such as alkyl phosphates and silicones; anti-redeposition
15 agents, such as sodium carboxymethyl cellulose and alkyl or substituted alkyl cellulose ethers; stabilizers, such as phosphonic acid derivatives (i.e. Dequest® types); fabric softening agents; inorganic salts and alkaline buffering agents, such as sodium sulphate, sodium silicate etc.; and
20 usually in very small amounts, fluorescent agents; perfumes; enzymes, such as proteases, cellulases, lipases, amylases and oxidases; germicides and colourants.

Experimental method

- 25 A 250 ml buffer solution was formed.

The pH of this solution was adjusted at 4, 7, 8.5, or 10 by using the required amount of acetate, bicarbonate, borate or phosphate, in combination with concentrated caustic or sulphuric acid. An aromatic aldehyde and other compounds,

- 30 were optionally added to the solution.

Subsequently, a BC-1 test-cloth was added to this solution and air, oxygen or argon (in an amount of 5-50ml/second) were bubbled through the solution at a temperature of 40°C for 2 hours.

- 35 The reflectance (R_{460}) of the BC-1 test cloth was measured on a Minolta CM 3700d colour measuring system including UV-

filter before and after this treatment. The difference (ΔR_{460}) between both reflectance values thus obtained gives a measure of the bleaching performance, i.e. higher ΔR_{460} values correspond to an improved bleaching performance.

5

The invention will now be further illustrated by way of the following non-limiting Examples.

Examples 1-2, Comparative Example A

- 10 The bleaching performance of a process according to the invention was compared with the bleaching effect of a process wherein the same type of aldehyde is applied (i.e. benzaldehyde) but wherein argon is used in stead of air. This comparison was carried out at pH of 4, 7, 8.5, and 10.

15

To each of a series of eight 250 ml buffer solution having one of the indicated pH-values, 0.5 ml of benzaldehyde and 50 mg of NHS were added. After insertion into the solutions of a BC-1 test cloth, three consecutive experiments were

- 20 carried out whereby air, oxygen and argon were bubbled through at 40°C for 2 hours.

As a result, the following ΔR values (showing the difference in reflection at 460 nm before and after treatment of the test cloth) were obtained.

25

<u>Example</u>	A	1	2
pH	Argon +	Air +	O ₂ +
	Benzaldehy/NHS	Benzaldehy/NHS	Benzaldehy/NHS
4	3.6	7.4	6.9
30 7	2.9	7.2	6.0
8.5	3.8	5.8	4.0
10	2.3	1.7	4.0

- It can be seen that at pH of 4, 7, 8.5 a significant bleach
35 benefit is obtained when applying the process of the invention.

Examples 3-7

The bleaching performance of the process of the invention was measured, whereby various types of aromatic aldehydes were used in said process.

- 5 A 250 ml buffer solution having a pH of 7 was formed. (The pH of said solution was adjusted at 7 by using 50 mM of phosphate.) To this solution, 0.5 ml of the tested type of aldehyde and 50 mg NHS were added. After insertion of A BC-1 test cloth into the solution, air was bubbled through at
10 40°C during 2 hours. This experiment was repeated for 5 different types of aromatic aldehyde.

As a result, the following ΔR -values were obtained for the various tested types of aldehyde.

15

<u>Example no.</u>	<u>Type of</u> <u>aromatic aldehyde</u>	<u>Delta R</u>
3	4-hydrogen benzaldehyde	5.3
20 4	4-methyl benzaldehyde	11.8
5	4-ethyl benzaldehyde	12.3
6	4-isopropyl benzaldehyde	10
7	2,4,6-trimethyl benzaldehyde	5.6

- 25 It can be seen that the best bleaching performance is achieved when using a benzaldehyde which is substituted on the para-position with a methyl or an ethyl group.

Example 8. Comparative Example B

- 30 The bleaching performance of the process of the invention on curry stained test cloths was demonstrated.

Two 250 ml buffer solutions having a pH of 7 were formed using the method of Examples 3-7. To these solutions, 0.5
35 ml of 4-methyl-benzaldehyde and 50 mg of NHS were added.

After insertion of a curry-stained test cloth into the solutions, air respectively argon were bubbled through at 40° C during 2 hours.

As a result, the following ΔR values were obtained.

5

<u>Example</u>	<u>B</u>	<u>8</u>
pH=7	Argon +	Air +
	4-methylbenzaldehyd./NHS	4-methylbenzaldehyd./NHS
	7.3	21.3

10

It can be seen that there is clearly also a significant bleaching result on curry-stained cloths when using the process of the present invention.

15 Example 9. Comparative Example C

The bleaching performance of the process of the invention on wine-stained test cloths (i.e. EMPA-114) was demonstrated.

20 A 250 ml buffer solution having a pH of 7 was formed using the method of Examples 3-7. To this solution, 0.5 ml of 4-methyl-benzaldehyde and 50 mg of NHS were added. After insertion of an EMPA-wine-stained test cloth into the solution, air was bubbled through at 40°C during 2 hours.

25

For reasons of comparison, air was also bubbled through a 250 ml buffer solution having a pH of 7 at 40°C during 2 hours, which comparative solution contained an EMPA test cloth but not the toluyaldehyde/NHS system.

30 As a result, the following ΔR values were obtained.

<u>Example no.</u>	<u>C</u>	<u>9</u>
	air	air +
		4-methylbenzaldehyd./NHS
35	14.6	18.0

It is noticeable that there is also a significant increase in bleaching performance on EMPA-wine-stained test cloths when applying the process of the present invention.

5 Examples 10-12

The effect of the addition to the wash liquor of ligand containing iron and manganese complexes on the bleaching performance of the process of the invention was demonstrated.

10

A series of two 250 ml buffer solutions having a pH of 10 was formed. The pH of said solutions was adjusted at 10 by using 50 mM borate.

To these solutions, 0.5 ml ethylbenzaldehyde and 1.5 micromol
15 of a specific type of manganese respectively iron complex (see below) was added. After insertion of a BC-1 test cloth into these solutions, air was bubbled through at 40°C during 2 hours.

20 For reasons of comparison, a third experiment was carried out whereby air was bubbled through a 250 ml buffer solution having a pH of 10, said solution containing a BC-1 test cloth and 0.5 ml ethylbenzaldehyde but not containing any transition metal complex.

25 As a result, the following ΔR values were obtained.

<u>Example no</u>	<u>Metal complex added</u>	<u>Delta R</u>
10	none added	9.6
11	$(L_2^1 Mn_2 O_3) \cdot (PF_6)_2$	18.6
30 12	$L^2 FeCl$	18.6

wherein:

L^1 : 1,4,7-trimethyl-1,4,7-triazacyclononane

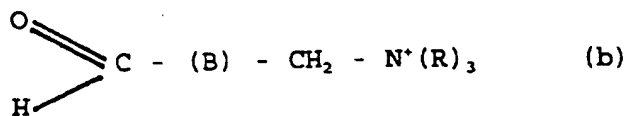
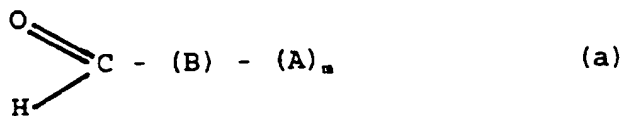
L^2 : N,N-bis(pyridin-2-yl-methyl)-bis(pyridin-2-yl)-
35 methylamine.

These data clearly show that the tested transition metal complexes have a strong positive effect on the bleaching performance of the process of the present invention.

CLAIMS

1. A process for cleaning of a substrate, comprising the steps of (1) adding a molecular oxygen activating system (as defined herein) to an aqueous wash liquor, containing a sufficient amount of molecular oxygen for obtaining observable cleaning, and
(2) cleaning the substrate with the thus-formed wash liquor.

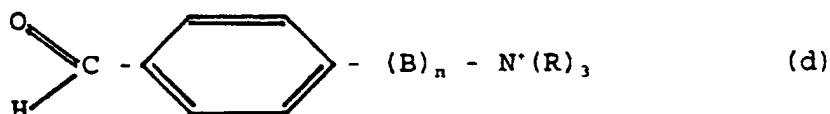
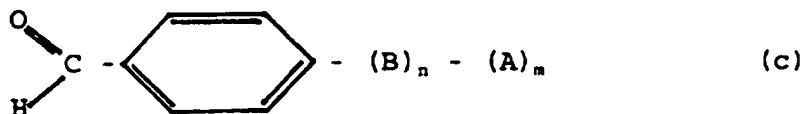
2. The process according to claim 1, wherein the activating system includes from 0.01 to 40 mMol/litre, based on the volume of the wash liquor, of at least one aldehyde according to the formulas (a) or (b):



wherein:

A is selected from sulphate, sulphonate, phosphate, carboxylate, nitro, amine, or a quaternary ammonium group; B and R are independently selected from C_1 - C_{10} branched or linear, substituted or unsubstituted alkyl, polyethoxy alkyl, hydroxyalkyl or an aromatic group selected from substituted or unsubstituted benzene, naphthalene, pyrrole, furane, thiophene, imidazole, pyrazole, pyridine, pyrimidine, indole or benzimidazole; and m is an integer which may be 0 or 1.

3. The process according to claim 2, wherein the aldehyde is an aromatic aldehyde according to the formulas (c) or (d):



wherein A, B, R, and m are defined as indicated in claim 2, and n is an integer which may be 0 or 1.

4. The process according to claim 3, wherein the aromatic aldehyde is a compound according to formula (c) wherein m is 0, n is 1, and B is a C₁-C₅, branched or linear, alkyl or alkoxy group.

5. The process according to claim 4, wherein the aromatic aldehyde is selected from 4-ethyl benzaldehyde and 4-methyl benzaldehyde.

6. The process according to any of claims 1-5, wherein the wash liquor contains at least 0.01 mMol/litre of molecular oxygen.

7. The process according to any of claims 1-6, wherein molecular oxygen is supplied to the wash liquor.

8. The process according to any of claims 1-7, wherein molecular oxygen is generated in situ by electrochemical, chemical or enzymatic reactions.

9. The process according to any of claims 1-8, wherein a radical initiator (as herein defined) is present in the wash liquor, at a concentration of 0.1 - 2 mmol/liter.

10. The process according to claim 9, wherein the radical initiator is selected from N-hydroxy-succinimide and benzoyl peroxide.

11. The process according to any of claims 1-10, wherein a transition metal complex is present in the wash liquor, at a concentration of 0.1-20 micromol/liter.

12. The process according to any of claims 1-11, wherein said process is carried out at a pH of from 4 to 12.

13. The process according to any of claims 1-12, wherein the substrate to be cleaned is a fabric.

14. Use of a molecular oxygen activating system for cleaning of a substrate, whereby said activating system is added to an aqueous wash liquor containing a sufficient amount of molecular oxygen for obtaining observable cleaning, and the substrate is cleaned using the thus-formed wash liquor.

INTERNATIONAL SEARCH REPORT

International Application No
PC/EP 97/01287

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/20 C11D11/00 C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 148 302 A (PROCTER & GAMBLE) 11 March 1973 see page 11, line 2-7 see page 14, line 38 - page 15, line 7 ---	1-3,8, 12-14
X	DATABASE WPI Week 8822 Derwent Publications Ltd., London, GB; AN 88-151591 XP002016737 & JP 63 092 698 A (KAO) , 23 April 1988 see abstract ---	1-4,14
X	DE 470 118 C (S.B. WEINMANN) 5 January 1929 see claim 2; example 1 ---	1,3,14
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

20 May 1997

Date of mailing of the international search report

29.05.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patendaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Van Bellinghen, I

INTERNATIONAL SEARCH REPORT

International Application No
PC1/EP 97/01287

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 125 103 A (PROCTER & GAMBLE) 14 November 1984 see page 8, last paragraph - page 9, line 3; claim 1 ---	1,2
X	EP 0 050 015 A (YUKEN INDUSTRIES) 21 April 1982 see claim 11 -----	1,2

1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 97/01287

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2148302 A	11-03-73	GB 1368400 A US 3822114 A AU 4535772 A CA 991364 A CA 993754 A CA 993755 A CH 574497 A DE 2238207 A NL 7210754 A SE 385718 A,B, US 4006092 A BE 787276 A ZA 7205311 A	25-09-74 02-07-74 14-02-74 22-06-76 27-07-76 27-07-76 15-04-76 15-02-73 07-02-73 01-02-77 07-02-73 25-04-73
DE 470118 C		NONE	
EP 125103 A	14-11-84	CA 1225300 A US 4547301 A	11-08-87 15-10-85
EP 50015 A	21-04-82	JP 57126897 A JP 1361575 C JP 57067699 A JP 61025784 B	06-08-82 30-01-87 24-04-82 17-06-86